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Electronic absorption spectra of hydrogenated protonated naphthalene and proflavine

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ABSTRACT

We study hydrogenated cations of two polycyclic hydrocarbon molecules as models of hydrogenated organic species that form in the interstellar medium. Optical spectra of the hydrogenated naphthalene cation H_n–$C_{10}H_8^+$ for $n = 1$, 2 and 10, as well as the astrobiologically interesting hydrogenated proflavine cation H_n–$C_{13}H_{11}N_3^+$ for $n = 1$ and 14, are calculated. The pseudopotential time-dependent density functional theory is used. It is found that the fully hydrogenated proflavine cation H_{14}–$C_{13}H_{11}N_3^+$ shows a broad spectrum in which the positions of individual lines are almost lost. The positions, shapes and intensities of lines change in hydronaphthalene and hydroproflavine cations, showing that hydrogen additions induce substantially different optical spectra in comparison with base polycyclic hydrocarbon cations. One calculated line in the visible spectrum of H_{10}–$C_{10}H_8^+$ and one in the visible spectrum of H–$C_{13}H_{11}N_3^+$ are close to the measured diffuse interstellar bands. We also present the positions of near-ultraviolet lines.

Key words: astrochemistry – molecular processes – methods: numerical.

1 INTRODUCTION

Hydrogen, in its atomic and molecular form, is the most abundant of chemical species in the interstellar medium. The number and size of detected interstellar molecules have been increasing over the last eighty years. Polycyclic aromatic hydrocarbons (PAHs) have been investigated as carriers of diffuse interstellar bands (DIBs), because of unidentified infrared (UIR) emission features and as a source of anomalous microwave emission (Tielens 2008). It has been suggested that protonated PAH molecules play a catalytic role in the process of H_2 formation in space (Bauschlicher 1998; Hirata et al. 2004). Electronic transitions in the optical spectral region of protonated hydrogenated coronene, ovalene, pyrene and circumpyrene have been recently calculated and discussed in the context of the DIBs problem (Pathak & Sarre 2008; Hammonds, Pathak & Sarre 2009). Spectra of isomers of protonated anthracene and phenanthrene have been measured in neon matrices and studied by the time-dependent density functional theory (Garkusha et al. 2011). We have selected here cations of naphthalene and proflavine to study the change of their overall optical spectra under additions of hydrogen atoms. The presence of $C_{10}H_8^+$ in the interstellar medium has been discussed (Iglesias-Groth et al. 2008; Galazutdinov et al. 2011). Several times in the past, evidence of the interstellar naphthalene cation was reported and later shown to be premature (Galazutdinov et al. 2011). Proflavine is a substituted PAH molecule with possible applications in astrophysics and astrobiology (Sarre 2006; Bonaca & Bilalbegović 2010).

A theoretical study of reactions has shown that the first H atom attaches to the naphthalene cation $C_{10}H_8^+$ in an exothermic reaction of about 60 kcal mol^{-1}, whereas the process for the second H atom is exothermic by 45 kcal mol^{-1} (Bauschlicher 1998). Herbst and Le Page have found that the naphthalene cation associates efficiently with atomic hydrogen at all densities (Herbst & Le Page 1999). Calculations have also shown that the addition of H atoms to the naphthalene cation proceeds with few or no barriers (Ricca, Bakes & Bauschlicher 2007). Electronic absorption spectra of H–$C_{10}H_8^+$ have been studied by photofragment spectroscopy and theoretical analysis (Alata et al. 2010a,b). It has been found that the protonated naphthalene cation absorbs in the visible part of the spectrum around 500 nm. A possibility that $C_{10}H_8$ and $C_{10}H_8^+$ are carriers of DIBs has been studied (Salama & Allamandola 1992; Hirata, Lee & Head-Gordon 1999; Krelowski et al. 2001; Malloci et al. 2007b). Evidence of the naphthalene cation in the direction of the star Cernis 52 in the Perseus molecular cloud complex has been reported (Iglesias-Groth et al. 2008). The presence of some known DIBs has been confirmed in this study, and two new bands consistent with laboratory measurements of the naphthalene cation have been observed. It has also been proposed that hydrogen additions produce hydronaphthalene cations, which contribute to the anomalous microwave emission in this cloud (Iglesias-Groth et al. 2008). However, a recent work (Galazutdinov et al. 2011) has shown that this report (Iglesias-Groth et al. 2008) is premature. The presence of the naphthalene cation and related species in the interstellar medium deserves further study.

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In addition to PAHs, the related molecules in which C and H are substituted by other atoms are also studied in an astrophysical context (Hudgins, Bauschlicher & Allamandola 2005; Sarre 2006). Nitrogen is abundant in the interstellar medium. Its compounds have been detected in interstellar dust particles and meteorites. The organic dye proflavine, $C_{13}H_{11}N_3$ (3,6-diaminoacridine), has been proposed as one of the molecules that act as molecular 'midwives' because of their property to accelerate DNA and RNA synthesis (Jain et al. 2004). Therefore, the optical spectrum of proflavine and its ions is of astrobiological interest. Studies of such large biological molecules are important for an understanding of prebiotic chemistry (Puletti et al. 2010). Organic dyes often exhibit strong lines in the visible spectrum. It has been shown that the optical spectrum of proflavine in aqueous solutions strongly depends on the pH value (De Silvestri & Laporta 1984; Homem-de Mello et al. 2005). Protons can attach to nitrogen and carbon atoms in the molecule, and the state of proflavine in water and other solvents depends on the pH of the solution. For example, it has been measured that the maximum of absorption in the visible spectrum of proflavine (λ_{max}) in water at room temperature changes from 444 to 394 nm when the pH changes from 7.0 to 14.0 (De Silvestri & Laporta 1984). The visible and UV optical spectra of proflavine and its ions have been recently studied using pseudopotential time-dependent density functional theory methods (Bonaca & Bilalbegović 2010). The positions of spectral lines have been compared with DIBs, but with no definite conclusions. Because of the sensitivity of the optical properties of proflavine in water to the pH factor, we investigated here the impact of hydrogen additions on the optical spectrum of its cation.

In this work we consider minimal and maximal hydrogenation of two organic cations. An addition of 1, 2 and 10 H atoms to the naphthalene cation, as well as 1 (in two positions) and 14 hydrogen atoms to the proflavine cation, is studied. We use pseudopotential density functional theory (DFT) (Martin 2004) to determine the ground states of all base and hydrogenated species. Calculations of the optical spectra of these systems within pseudopotential time-dependent density functional theory (TDDFT) methods (Runge & Gross 1984) are described in Section 2. Our results are presented and discussed in Section 3, while final remarks are given in Section 4.

2 COMPUTATIONAL METHODS

Optical spectra are calculated using the OCTOPUS code (Castro et al. 2006). The geometries of all naphthalene and proflavine systems are minimized independently by the QUANTUM ESPRESSO DFT package (Giannozzi et al. 2009). This approach is taken because of the fact that OCTOPUS is not in general suitable for a search of optimal geometries. Conditions as close as possible to simulations of the spectra within the OCTOPUS code have been used in the Quantum ESPRESSO calculations (i.e. the local density approximation (LDA) and corresponding pseudopotentials, see below and in Bonaca & Bilalbegović 2010). The optimized geometries of cations are calculated without imposing any constraints, and they are used as inputs in the ground state and time-dependent calculations in the OCTOPUS code.

Optical spectra are obtained using a time-propagation method and the approximated enforced time-reversal symmetry algorithm (Castro, Marques & Rubio 2004). The ground state is perturbed by an impulsive time-dependent potential and the time evolution is followed for 15.8 fs. In the time-propagation TDDFT method used in this work, the width of spectral lines is inversely proportional to the total propagation time (Marques et al. 2003; Castro et al. 2006; Malloci et al. 2007b; Puletti et al. 2010). A step of $0.0012\,\hbar\,\mathrm{eV}^{-1}$ is applied. The absolute cross-section $\sigma(\omega)$ is obtained from the dynamical polarizability $\alpha(\omega)$, which is calculated from the Fourier transform of the time-dependent dipole momentum of the system. Electronic spectra are calculated from

$$\sigma(\omega) = \frac{2\omega}{\pi}\Im\,\alpha(\omega). \quad (1)$$

In this equation $\Im\,\alpha(\omega)$ is the imaginary part of the dynamical polarizability. The Troullier–Martins pseudopotentials (Troullier & Martins 1993) and the TDLDA approximation with the Perdew–Zunger exchange-correlation functional (Perdew & Zunger 1981) are used, as well as a spacing of 0.13 Å in the real-space method. The simulation cell is constructed from spheres of 4 Å radii around atoms. The TDLDA approximation in the pseudopotential TDDFT method shows very good stability and produces results in agreement with experiments, even for large biological molecules (Marques et al. 2003). It has been found that the results of TDDFT calculations (within the Tamm–Dancoff approximation and using the Becke–Lee–Yang–Parr (BLYP) functional) for the excitation energies of several PAH cations agree with experiments to within 0.3 eV (Hirata et al. 1999). We have found that calculations with the B3LYP functional (still in development in the latest version of the OCTOPUS code) do not change the spectrum of proflavine substantially (Bonaca & Bilalbegović 2010). It has also been found that spectra of proflavine obtained using the time-propagation method in the OCTOPUS code agree with the results of the Lanczos-chain TDDFT module in Quantum ESPRESSO (Walker et al. 2006; Bonaca & Bilalbegović 2010). It is known that the real-time propagation method of the OCTOPUS code produces the whole optical spectrum up to the far-UV (Castro et al. 2006). However, for energies above 10 eV only envelopes of the spectra are accurate. In addition, there is little astronomical interest in the high-energy region of the spectrum. To facilitate a comparison with other studies of PAHs and organic molecules of astrophysical interest carried out by the same TDDFT method (Malloci, Joblin & Mulas 2007a; Malloci et al. 2007b; Bonaca & Bilalbegović 2010; Puletti et al. 2010) we show optical spectra up to 6 eV.

The hydronaphthalene cation $C_{10}H_9^+$ and the dihydronaphthalene cation $C_{10}H_{10}^+$, with additional H atoms attached at the same positions as in Bauschlicher (1998), are studied. Two situations of minimal hydrogenation, where one hydrogen atom is added to the proflavine cation, are also investigated here: an additional H atom attached as the second hydrogen atom at the central carbon atom (labelled as (I)) and at the opposite nitrogen atom in the same central ring (labelled as (II)). We also study fully hydrogenated species of naphthalene and proflavine cations: H_{10}–$C_{10}H_8^+$ and H_{14}–$C_{10}H_{13}N_3^+$.

3 RESULTS AND DISCUSSION

The optimized structures of all investigated species of naphthalene and proflavine are shown as insets in Figs 1–3. In contrast to the naphthalene and proflavine molecules, carbon skeletons of fully hydrogenated H_{10}–$C_{10}H_8^+$ and H_{14}–$C_{13}H_{11}N_3^+$ (shown in Figs 2c and 3c) are not planar. In addition, hydrogen atoms attached in pairs on peripheral carbon atoms are positioned below and above the middle plane of carbon rings. Average C–C distances increase from 1.39 Å in the optimized naphthalene cation to 1.51 Å in H_{10}–$C_{10}H_8^+$. Average N–C distances increase from 1.34 Å in $C_{13}H_{11}N_3^+$ to 1.41 Å in H_{14}–$C_{13}H_{11}N_3^+$. Average C–C distances increase from 1.40 Å in the proflavine cation to 1.51 Å in H_{14}–$C_{13}H_{11}N_3^+$. Hydrogen atoms are also attached to the C atoms in pairs above and below rings

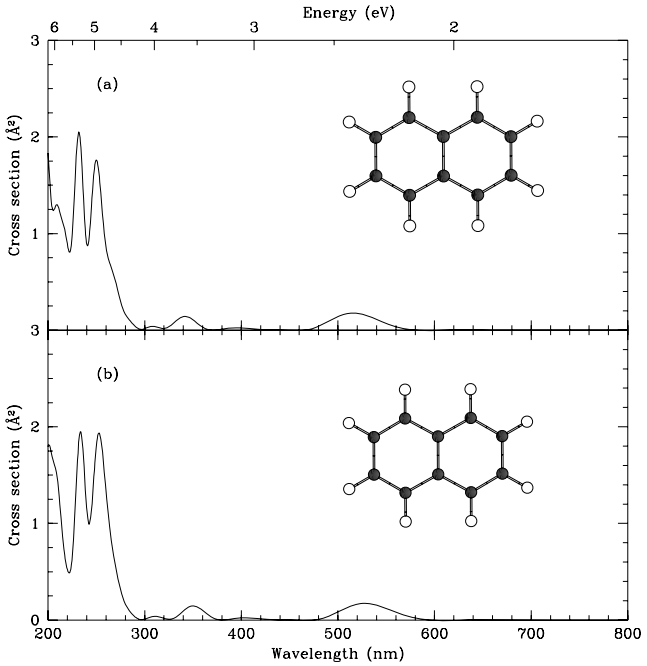

Figure 1. Optical spectra of the naphthalene cation: (a) after geometry optimization without constraints, (b) for the cation with the optimized structure of neutral naphthalene. Insets: black circles represent carbon atoms, whereas white ones model hydrogen atoms. Structures are visualized using the XCRYSDEN program (Kokalj 2003).

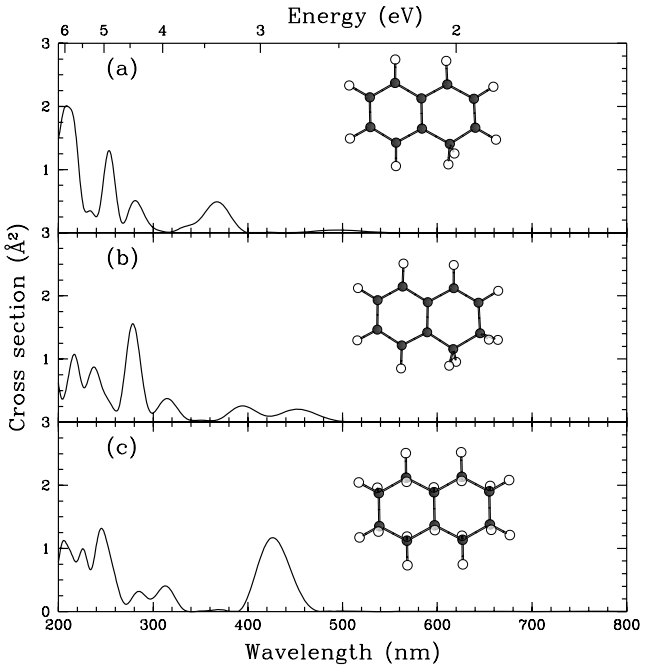

Figure 2. Optical spectra of hydrogenated species of naphthalene cation: (a) H–$C_{10}H_8^+$, (b) H_2–$C_{10}H_8^+$, (c) H_{10}–$C_{10}H_8^+$.

in optimized H–$C_{10}H_8^+$ (one pair, inset in Fig. 2a) and H_2–$C_{10}H_8^+$ (two pairs, inset in Fig. 2b). However, carbon skeletons are planar in both these structures with minimal hydrogenation, as well as in H–$C_{13}H_{11}N_3^+$ (in both positions I and II, insets in Fig. 3a and b). A similar conclusion regarding the planarity of H–$C_{10}H_8^+$ has been reached by Alata et al. (2010a).

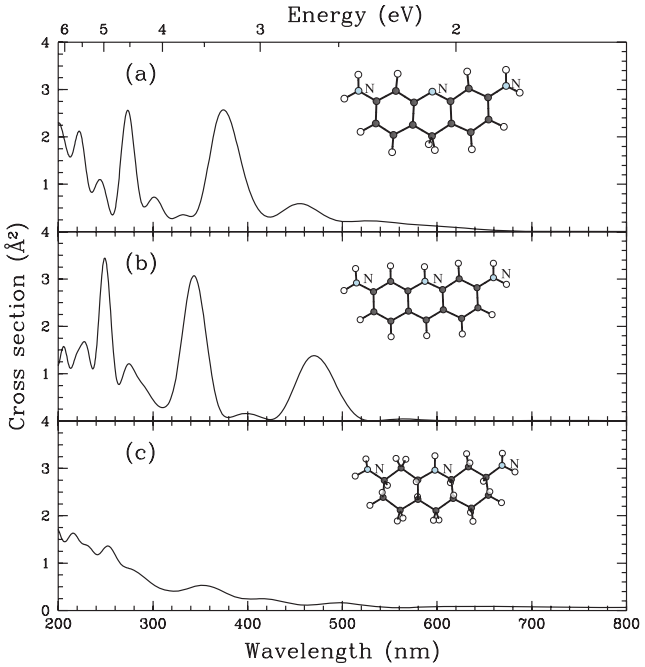

Figure 3. Optical spectra of hydrogenated species of proflavine cation: (a) H–$C_{13}H_{11}N_3^+$, additional H atom attached at the central C atom (position I), (b) H–$C_{13}H_{11}N_3^+$, additional H atom attached at the central N atom (position II), (c) H_{14}–$C_{13}H_{11}N_3^+$. Insets: nitrogen atoms are labelled by 'N' on the right-hand side of the corresponding filled circles.

Optical spectra presented in this work are calculated starting from structures optimized separately for all pure and hydrogenated cations, and without any constraints in geometrical optimizations. We found that the fully optimized naphthalene cation is still a planar structure. However, the charge and small displacements from the atom positions of neutral naphthalene produce small differences in the spectrum. Optical spectra for the fully optimized cation and the structure in which one electron is removed from the optimized geometry of neutral naphthalene (Niederalt, Grimme & Peyerimhoff 1995; Hirata, Lee & Head-Gordon 1999; Malloci et al. 2007b) are shown in Fig. 1. The geometry used as an input for Fig. 1(b) is taken from the theoretical spectral data base of PAHs (Malloci et al. 2007a). Our result for the optical spectrum of the naphthalene cation in this situation agrees with that presented in the data base (Malloci et al. 2007a). Lines for spectra shown in Fig. 1 are compared in Table 1.

Optical spectra of hydrogenated protonated naphthalene species are shown in Fig. 2. Peaks of the naphthalene cation move in H–$C_{10}H_8^+$, H_2–$C_{10}H_8^+$ and H_{10}–$C_{10}H_8^+$ and their intensities change.

Table 1. Optical spectral lines of the naphthalene cation and hydrogenated naphthalene cation species. The star labels data for the naphthalene cation with the optimized geometry of the neutral naphthalene molecule, whereas all other data are obtained for optimized cations. Because of the limited accuracy of the TDDFT method, the calculated results are presented rounded to whole numbers.

Structure	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)	λ_5 (nm)	λ_6 (nm)
$C_{10}H_8^+$	200.	232.	250.	342.	517.	-
$C_{10}H_8^+$ (*)	201.	234.	253.	350.	528.	-
H–$C_{10}H_8^+$	209.	233.	254	281.	367.	494.
H_2–$C_{10}H_8^+$	217.	238.	279.	315.	395.	453.
H_{10}–$C_{10}H_8^+$	206.	226.	246.	285.	313.	426.

Table 2. Optical spectral lines of proflavine cation and hydrogenated proflavine cation species. Labels (I) and (II) are for H atoms attached to the central carbon and central nitrogen atom respectively. Because of the limited accuracy of the TDDFT method, the calculated results are presented rounded to whole numbers.

Structure	λ_1 (nm)	λ_2 (nm)	λ_3 (nm)	λ_4 (nm)	λ_5 (nm)	λ_6 (nm)	λ_7 (nm)	λ_8 (nm)
$C_{13}H_{11}N_3^+$	281.[1]	422.[1]	-					
H–$C_{13}H_{11}N_3^+$ (I)	201.	222.	244.	273.	301.	332.	375.	454.
H–$C_{13}H_{11}N_3^+$ (II)	206.	228.	249.	274.	343.	399.	470.	-
H_{14}–$C_{13}H_{11}N_3^+$	216.	253.	352.	420.	496.	-	-	-

[1](Bonaca & Bilalbegović 2010).

Optical spectra of hydrogenated protonated proflavine species are shown in Fig. 3. The most notable fact is that the spectrum of H_{14}–$C_{13}H_{11}N_3^+$ (Fig. 3c) is broad and this broadening is much more pronounced than in fully hydrogenated naphthalene (Fig. 2c).

Spectral lines of all naphthalene- and proflavine-related systems are presented in in Tables 1 and 2. Visible spectra of hydrogenated naphthalene cations extend up to ∼500 nm, whereas the long tails of the visible spectra of hydrogenated proflavine cations spread above 800 nm. The photofragmentation spectroscopy measurements by Alata and coworkers have also shown that H–$C_{10}H_8^+$ absorbs in the visible, around 500 nm (Alata et al. 2010a,b). We also present near-UV lines (above 200 nm) to facilitate a comparison with corresponding spectral measurements of interstellar organic materials (Kwok & Sanford 2008). Such experiments are designed to be carried out on the Cosmic Origins Spectrograph (COS) of the *Hubble Space Telescope* (Osterman et al. 2011). The near-UV channel of COS shows a high sensitivity in the region between 200 and 300 nm where lines of hydrogenated protonated naphthalene and proflavine exist. The lines at 281 and 422 nm in the spectrum of the proflavine cation [Bonaca2010] move to 273 and 454 nm, and three new lines appear between these two in the spectrum of H–$C_{13}H_{11}N_3^+$ (position I). Rather strong lines exist at 201, 222 and 244 nm. An addition of the H atom to the central N atom produces lines between 206 and 470 nm, as shown in Table 2. The change of optical lines is most obvious in the spectrum of H_{14}–$C_{13}H_{11}N_3^+$, where UV lines exist at 216 and 253 nm. The intensity then drops, and the lines at 352, 420 and 496 nm are very weak.

It is known that the majority of DIBs are present in atomic hydrogen gas (Herbig 1993; Snow & McCall 2006). In Table 3 we compare the positions of several calculated lines with the closest DIBs (Hobbs et al. 2008, 2009; Tuairisg et al. 2000). The best agreement is for a line of the fully hydrogenated naphthalene cation $H_{10}C_{10}H_8^+$ and a line of H–$C_{13}H_{11}N_3^+$ (position II). Although TDDFT calculations show only trends in DIB positions (Malloci et al. 2007a,b; Pathak & Sarre 2008; Hammonds et al. 2009), the agreement presented in Table 3 is good and deserves further experimental investigation. In the recent report of high-resolution spectroscopy observations of $C_{10}H_8^+$ in Cernis 52, the importance of hydronaphthalene cations has been pointed out (Iglesias-Groth et al. 2008). Although this report has been shown to be premature (Galazutdinov et al. 2011), the presence of the naphthalene cation and its hydrogenated forms in the interstellar medium remains an important subject for further investigation.

Table 3. Lines calculated using the time-dependent density functional theory (TDDFT) method compared with the nearest DIBs. Because of the limited accuracy of the TDDFT method, the calculated results are presented rounded to whole numbers. The full widths at half-maximum (FWHM) of experimental lines are also shown.

Structure	λ(TDDFT) (nm)	λ(DIB) (nm)	FWHM (nm)
$C_{13}H_{11}N_3^+$	422.[1]	417.55[2]	1.72
H–$C_{13}H_{11}N_3^+$ (I)	454.	450.17[3]	0.30
H–$C_{13}H_{11}N_3^+$ (II)	470.	476.26[3]	0.25
$H_{10}C_{10}H_8^+$	426.	425.90[4]	0.11

[1](Bonaca & Bilalbegović 2010).
[2](Tuairisg et al. 2000).
[3](Hobbs et al. 2009).
[4](Hobbs et al. 2008).

4 CONCLUSIONS

Studies of spectra of polycyclic aromatic hydrocarbon cations with attached hydrogen atoms are important for DIB and UIR problems and anomalous microwave emission, as well as for the general properties of organic matter in the interstellar medium. We study the changes in electronic absorption spectra induced by hydrogen additions to the naphthalene and proflavine cations using the time-dependent density functional method in its pseudopotential version. Calculated spectra are based on the overall density of electronic transitions and show that hydrogen additions substantially change the intensities, shapes and positions of optical lines in comparison with spectra of base cations. Therefore, addition of hydrogen atoms is important in astrophysical applications of optical spectra of organic molecules. Similar conclusions have been found for protonated hydrogenated coronene, ovalene, pyrene and circumpyrene (Pathak & Sarre 2008; Hammonds et al. 2009). Calculated lines of protonated hydrogenated naphthalene and proflavine are compared with measured DIBs. An especially good agreement exists for the visible line of the fully hydrogenated naphthalene cation and two visible lines of the hydroproflavine cations. The lines in the near-UV spectral region are also presented. Our calculations should give guidelines regarding the change of near-UV and visible spectral lines for similar large cations and their derivatives under the process of hydrogenation.

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